

Therefore, M is the balance point of an equi-weighted centroid and coincides with C . The slope of the line AB is

$$3 \left(\frac{\bar{y}_B - \bar{y}_A}{n-1} \right)$$

and that of the best fitting line is $\Sigma xy / \Sigma x^2$.

Substituting the proper values gives

$$3 \left(\frac{\Sigma n_i y - \Sigma [y(n+1-n_i)]}{\Sigma n_i} \right) = \frac{\Sigma xy}{\Sigma x^2} \quad (3)$$

When n is odd, Eq. 3 leads through

$$\frac{\Sigma n_i}{2} \left(\Sigma \left[y \left(x + \frac{n+1}{2} \right) \right] - \Sigma \left[y \left(\frac{n+1}{2} - x \right) \right] \right) = \Sigma xy \Sigma \left(x + \frac{n+1}{2} \right) \quad (4)$$

to

$$\Sigma n_i \Sigma xy = \Sigma n_i \Sigma xy$$

When n is even, Eq. 3 leads through

$$2 \Sigma [y(x+n+1)/2] - (n+1) \Sigma y = \Sigma xy \quad (5)$$

to

$$\Sigma xy = \Sigma xy$$

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Gases in Icebergs

Pure ice in thick layers is bluish in color, whereas an iceberg is typically white. The whiteness is caused by tiny, closely spaced gas cavities that are dispersed all through the ice. The cavities are often elongated and oriented lengthwise; this gives a grain to the ice. The gas is usually under pressure and is liberated with a fizzing sound when a piece of berg ice melts in a pail of water. With a lens one may watch the bubbles suddenly enlarge and pop out of their cavities when the walls melt open. The pressure is also manifested by the way chips almost fly off the ice at the slightest fracture. This is undoubtedly caused by the release of compressed air from the bubbles into the fracture.

Either the gas bubbles in a iceberg could be atmospheric air trapped at the time snow was compacted into glacier ice, or, since gases are insoluble in ice (1), the bubbles could be frozen out of air-saturated water, as they are in ice cubes from a refrigerator. Water equilibrated with air at 0°C contains 2.9 percent by volume of dissolved gases, of

which 34.9 percent is oxygen. Since air has only 20.9 percent oxygen, the concentration of this gas in the bubbles may tell whether the ice was formed by compacting the snow crystals or by freezing of a body of water (2).

The rate of gas diffusion through ice is no more than 1/40,000 to 1/70,000 as fast as it is through water (1). Considering this extremely slow rate, the relatively enormous diffusion distances in the glacier, and the large quantity of gases held under pressure in the ice, it would seem possible that gas trapped in the glacier would remain unchanged for millennia. Analysis of such gas could therefore give information about the atmospheric composition at the time the ice was formed.

This article (3) presents studies on pieces of icebergs taken on board the research vessel *Blue Dolphin* along the Labrador coast. Most icebergs in this area are of Greenland origin. In the interior of Greenland and the Antarctic, the temperature stays below freezing all year, and the glacier ice is formed by the compacting of snow under high pressure. These are the high polar glaciers. In glaciers of warmer climates, melt water percolates through the snow in the summer and freezes deeper down, as an important part of the firnification process (4). The gas in such ice should accordingly be more or less enriched with oxygen. Only the polar type of glacier would therefore seem suitable for possible clues to the composition of ancient atmospheric air. Isotope distribution could probably be studied in either type.

Although the techniques for obtaining samples from bubbles in icebergs have been generally adequate, the composition of the gas has been found by several authors to be more or less close to that of the atmosphere, and it has long been known that the gas is usually under pressure (5). In our work, we melted a piece of ice in mercury. The gas phase and the dissolved gases in the melt water were analyzed separately and the results were totaled.

A piece of berg ice was shaved to fit

snugly into the barrel of a 20-ml syringe. The plunger was set in and mercury drawn in to cover the ice. The first milliliter of melt water and bubbles was discarded. The nozzle was closed with the finger, and the ice-and-mercury volume was read. The ice was quickly melted and a new volume reading taken. The gas phase was transferred to a tuberculin syringe to determine the volume, and it was analyzed for composition (6). The volume of meltwater w and mercury was read on the syringe and 1 ml of water was analyzed for dissolved oxygen and nitrogen (7). Carbon dioxide could not be determined accurately with the methods we had available. About 85 percent of the total amount of gas analyzed was in the gas phase.

The pressure of the gas in the ice was found as

$$g/x$$

where x is the volume of the compressed gas in the ice and g is the volume at 1 atm. This can be computed according to the formula

$$g/x = \frac{g}{v - 1.091w}$$

where v is the volume of ice and bubbles and 1.091 w is the volume of ice alone.

It can be estimated that the combined accuracy of the various measurements will amount to about ± 0.2 percent by volume for the total oxygen and nitrogen. The pressure estimates are probably valid to within ± 25 percent.

Thirty pieces taken from six different icebergs were analyzed. It will be seen from Table 1 that the oxygen content in all of the bergs is close to that of the atmosphere, that is, 20.9 percent. Nevertheless, the oxygen content of iceberg No. 5 and especially No. 6 was significantly lower. One may speculate that when the snow settled on the Greenland icecap ages ago and compacted into these pieces of glacier ice (No. 5 and No. 6), an atmosphere was trapped that is slightly lower in oxygen content than our present atmosphere (8). Possibly this ice was formed as far back as Pleistocene time, when cold climates may

Table 1. Gases in iceberg ice. Air-equilibrated water at 0°C contains 2.9 percent gas by volume, of which 34.9 percent is oxygen. Clear ice contains less than 0.003 percent gas, most likely none at all (1). The pressure determinations are based upon from two to eight analyses in each iceberg.

Iceberg No.	Ratio of compressed gas to ice (ml/100 ml)	Ratio of gas at 1 atm to melt water (ml/100 ml)	Gas pressure in ice (atm)	O ₂ in gas (%)
1	1.9 to 2.2	4.2 to 8.3	2.9 to 3.9	21.4, 21.2, 21.2
2	2.3 to 3.8	7.7 to 11.1	2.3 to 3.9	20.9
3	1.2 to 2.2	4.8 to 9.3	2.0 to 6.2	21.2
4	1.1 to 2.6	2.9 to 6.5	1.0 to 5.0	20.6
5	1.0 to 2.4	2.2 to 8.8	3.3 to 5.8	20.2, 20.4
6	2.1 to 5.2	5.6 to 9.9	1.7 to 2.6	20.0, 20.0, 20.1, 20.1

have curbed photosynthetic activity of green plants over large parts of the earth, resulting in a slight lowering of the oxygen content of the air. Such a hypothesis can be verified only by better determinations of the diffusibility of gases through ice and by more accurate laboratory procedures for the extraction and analysis of the gas. No particulate matter could be detected in our ice pieces, but we cannot exclude the possibility of oxygen loss from dust oxidation. Whether or not enough organic material can be obtained from the ice for radiocarbon dating we do not know.

In our random investigation we did not encounter ice with gas bubbles rich in oxygen, which is suggestive of frozen, air-saturated water such as one might encounter in temperate-type glacier ice.

The bubbles in our icebergs were found to be under pressure, usually between 2 and 6 atm. Why the pressure seems to vary so much from one part of a berg to another is a puzzling problem. If such pressure gradients can persist in the bergs for a long time they might reflect something of the history of the berg such as the depth in the glacier from which it came.

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References and Notes

1. P. F. Scholander *et al.*, *J. Cellular Comp. Physiol.* **42**, suppl. 1 (1953).
 2. Distilled water equilibrated at 20°C with air was frozen in a horizontal, rotating tube so that the gas and a small amount of unfrozen water collected in the center. The gas phase held 32.6 percent oxygen as against a theoretical value of 34.0 percent. The deficit undoubtedly remained dissolved in the unfrozen water.
 3. Contribution No. 818 from the Woods Hole Oceanographic Institution. This work was carried out on the *Blue Dolphin* Labrador Expedition, 1954, under the auspices of the Arctic Institute of North America, project ONR-138, with funds provided by the Office of Naval Research.
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 8. Analyses of the air at Point Barrow, 71°N, in Alaska showed it to be constant throughout the year and exactly the same as air in southern latitudes, namely, 20.94 percent oxygen. R. J. Hock *et al.*, *J. Meteorol.* **9**, 441 (1952).
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Synthesis of Coffinite—USiO₄

A recent communication by Stieff, Stern, and Sherwood (1) gave a preliminary description of a new mineral, coffinite (USiO₄), which has become recognized as a major uranium mineral on the Colorado Plateau. Coffinite is described as a fine-grained black mineral; it is best identified by its x-ray powder pattern. The crystal structure is tetragonal, isomorphous with thorite (ThSiO₄). It was also noted that all attempts to synthesize USiO₄ had been unsuccessful to date. We have spent some time on attempts to prepare USiO₄, and our work has now progressed to the point where a preliminary report can be made describing the synthesis of coffinite by a hydrothermal process (2). The synthetic coffinite has been identified by its crystal structure, even though pure material suitable for chemical analysis has not been isolated.

Our procedure is, briefly, as follows: 1 mmole each of uranium tetrachloride and sodium metasilicate are dissolved in 10 ml of water. Sodium hydroxide solution is added dropwise to the uranium-silicate solution until a stiff gel forms near the neutral point. Enough additional base is added to make the mixture slightly alkaline (pH 8 to 10) (3). The gelatinous precipitate is then centrifuged and transferred to a vitreous silica tube, which is placed in an Inconel bomb tube. We carry out these operations in a nitrogen atmosphere to prevent oxidation of the uranium. Whether this precaution is necessary remains to be determined. Other variables in the procedure must also be evaluated. The sealed Inconel tube is heated 4 to 5 days at 250°C to crystallize the USiO₄.

Synthetic coffinite appears as a bluish-green solid in the reaction products. The material prepared to date appears to be isotropic under the microscope, but x-ray powder patterns confirm the presence of tetragonal crystals of coffinite. Quartz or cristobalite have been identified as contaminants in all the coffinite preparations that have been made to date. A comparison of lattice dimensions of natural coffinites with the synthetic material gives the following: Arrowhead Mine (1), Mesa County, Colo., $a = 6.93$ kx, $c = 6.30$ kx; Jack Pile Mine (4), Laguna, N. M. (AE1019), $a = 6.937$ kx, $c = 6.285$ kx; and synthetic coffinite (5) $a = 6.977$ kx, $c = 6.307$ kx. The refractive index of synthetic coffinite has been found to be 1.83 to 1.85.

We have heated the black, naturally occurring coffinite (AE1019) in air at 375°C to oxidize away the organic matter with which it is associated. The inorganic residue retains the tetragonal structure, but is then a gray-green color that is characteristic of tetravalent uranium

compounds and quite similar to that of the synthetic coffinite.

Naturally occurring USiO₄ is reported (6) to decompose to UO₂ and amorphous silica when it is heated above 400°C, although Grüner (7) reports retention of the tetragonal structure of the Jack Pile Mine coffinite on ignition to 500°C. Our synthetic coffinite has been found to be thermally stable, in vacuum, for at least 5 hours at 700°C.

Work on coffinite, its preparation and its properties, is continuing and will be reported in more detail at a later date.

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References and Notes

1. L. R. Stieff, T. W. Stern, A. M. Sherwood, *Science* **121**, 608 (1955).
2. This work was performed under the auspices of the U.S. Atomic Energy Commission.
3. Our reaction products have invariably been UO₂ and silica whenever the mixture is allowed to remain slightly acidic during the heating process.
4. This sample was obtained through the courtesy of J. W. Grüner of the University of Minnesota.
5. Cell constants of the Jack Pile Mine and synthetic coffinite were measured by S. Siegel.
6. L. R. Stieff, personal communication.
7. J. W. Grüner, personal communication.

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Interference in Salkowski Assay of Indoleacetic Acid

The Salkowski reaction (1) has long been used as a simple assay for indole derivatives (2), although it is not entirely specific for them. In their study of the enzymatic destruction of growth substances, Tang and Bonner (3) utilized the Salkowski reaction as an assay for indoleacetic acid (IAA), one of the few compounds that gives a carmine-pink color with the reagent (2). Lately the reaction, especially in the modification of Gordon and Weber (4), has been widely used for the assay of IAA and other indole-containing growth substances, both in solution and on paper chromatograms. The colored product has recently been ascribed to hydroxylation of the indole nitrogen (5).

The assay method is, however, subject to interference from various sources. Siegel and Weintraub (6) and others have noted that peroxides interfere by making the pink color too fugitive to be measured, and Brauner (7) observed that the reaction is inhibited by light. The experiments described in this report show that a number of other commonly occurring compounds may regularly interfere with the assay and that important changes are caused by exposure to light during, before, or after color development (8).